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WO 96/23051 A1 US 4731194 A
Derwent Abstract No.1997-498579 [46] relating to JP920035596 (Neos) 09.09.1997

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(54) Abstract Title
Cleaning compositions

(57) Cleaning compositions including a photocatalytic or photochemically active material and a sensitising dye deposit a residue of the material on a surface. The residue effects decomposition at soils on the surface. The photocatalytic material may be titanium dioxide or zinc oxide.

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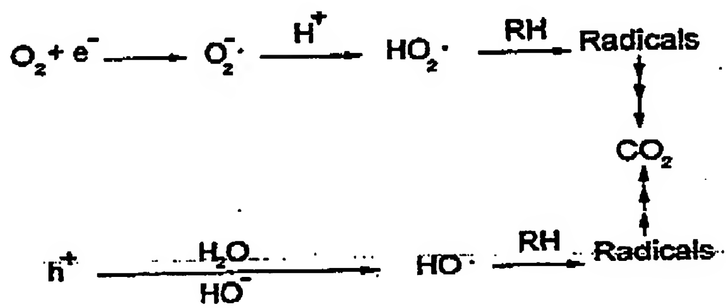


Figure 1

IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOSITIONS

The present invention relates to cleaning compositions and in particular to cleaning compositions intended to reduce the frequency and/or effort of cleaning; and to methods employing the cleaning compositions. The compositions of the invention are particularly suitable for cleaning hard surfaces such as ceramic tiles, sinks, baths, washbasins, toilets, worksurfaces, ovens, hobs, floors, painted woodwork, metalwork, laminates, glass surfaces and the like.

Cleaning compositions intended for general and for specific uses are well known in the art. Such compositions will commonly comprise (in an aqueous solution) one or more surfactants, to loosen and/or dissolve oily deposits and to dissolve water soluble materials. These cleaning compositions may further include one or more of solvents, thickening agents, abrasive particles, bleaching agents, disinfectants/antibacterial agents, perfumes, preservatives, colouring agents and like additives. The liquid formulation provides a vehicle for the removal of insoluble particulate matter and builders and suspending agents are often included in the compositions to facilitate this process. These prior art compositions are, to a greater or lesser extent,

effective in removing soils, usually organic soils, from surfaces and in preventing their redeposition during the cleaning process. However, re-soiling of the surfaces after cleaning is an inevitable and continuous process.

Thus, domestic and other surfaces are continually dirtied or soiled by various means including, for example, soiling resulting from the preparation of food, contact by people and domestic pets, deposition of oily deposits and of airborne materials. Not only are these and like soils aesthetically displeasing, ~~they may also have deleterious effects on health.~~ The soils may contain allergenic material such as pollen, dust mites, dust mite droppings, cat and other animal allergens and furthermore may include harmful or toxic materials derived from adjacent or nearby industrial, horticultural or agricultural processes. Deposited soils may also harbour and give sustenance to pathogenic micro-organisms or might include residues of human or animal faeces or urine. It is therefore important that these and like deposited soils are removed from surfaces efficiently and frequently.

Cleaning of surfaces is therefore a frequent and often time consuming requirement and is inevitably regarded as an unpleasant chore. There is a need for means to reduce the frequency of cleaning, and desirably also to facilitate the removal of soils deposited on surfaces. It will be appreciated that known, conventional, cleaning compositions have no effect on soils deposited on the surfaces after the

cleaning process until such time as the cleaning process is undertaken again. The present invention therefore seeks to provide cleaning compositions which, after the cleaning process, are effective to reduce the required frequency of cleaning and/or to facilitate the removal of deposited soils.

It is an object of embodiments of the invention to provide a cleaning composition which, in addition to removing existing soils deposited on a surface, also deposits on the surface a residue or layer which is preferably microscopic and which acts to decompose new soils which are deposited on the surface after cleaning.

In accordance with a first aspect of the present invention there is provided a cleaning composition comprising a photocatalytic material able to combat soils or a precursor to such a photocatalytic material, and a sensitising dye which acts to absorb visible or ultra-violet radiation and improve the efficacy of the photocatalytic material in combating soils.

By "combat" we mean that the cleaning composition can be used to remove and/or break down soil deposits and/or it can prevent soils from depositing and/or from building up.

The cleaning materials may have a deodorising effect, by breaking down odoriferous compounds, as deposits and/or as airborne compounds.

Thus, by means of the present invention a residue or layer of photocatalytic material can be provided on a surface whereby organic soils deposited on the residue or layer or soils which are present on the surface prior to deposition of the residue or layer are subject to a photocatalytic or other photochemical oxidation, reduction, free radical or other photochemical reaction effective to break down, "burn away" or otherwise decompose the soils or at least major components thereof; and/or to weaken their contact with the surface. Consequently it may be said ~~that the cleaning process continues after the~~ conventional act of soil removal is completed.

Where the photocatalytic material is a so-called optical catalyst, the decomposition reaction on the soil may involve photo-induced oxidation and/or photo-induced reduction reactions with organic or inorganic components of the soil. These reactions may in turn result in the production of free radicals which are effective in breaking down organic matter in the soils. These reactions may also provide an ongoing antibacterial effect which continues after the physical cleaning process has been completed.

One suitable photocatalytic material is titanium dioxide and a possible mode of action using titanium dioxide is described below, in conjunction with Figure 1 which illustrates this possible radical decomposition mechanism.

Whilst we are not bound by any scientific theory, in this suggested mode of action, incident light of appropriate energy can promote an electron from a valence band of the titanium dioxide to a conductance band. There is then an electron (e^-) in the conductance band and a hole (h^+) in the valence band. Both the electron and the hole may migrate to the surface of the titanium dioxide particle and interact with oxygen and water to product radical species (see Figure 1). These radical species may then generate free radical decomposition reactions in the organic soil which may ultimately generate carbon dioxide if the free radical reaction continues to its conclusion. It is believed that the sensitising dye is able to absorb light from the visible or ultra violet, preferably the visible, region which causes an excitation of the dye. Electrons are then emitted as the dye decays or decomposes from the excited state, and these electrons are transferred to the conductance band of the photocatalytic material, such as titanium dioxide.

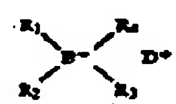
Thus there is also provided a cleaning composition which comprises:

a) a photocatalytic material able to combat soils or a precursor to such a photocatalytic material; and

b) a sensitising dye which is capable of absorbing radiation of a first wavelength from sunlight and emitting radiation of a second wavelength which enhances the cleaning effect of the photocatalytic material.

Preferably, the dye is present in an amount up to 1%, more preferably up to 0.1%, still more preferably up to 0.02%, and yet more preferably up to 0.01%. Preferably it is present in an amount of from 0.0001%, more preferably from 0.003%, and most preferably from 0.001%.

There are many sensitising dyes which will improve the efficacy of the photocatalytic material. Examples may include cationic, anionic, non-ionic and amphoteric dyes. Cationic dyes are preferred. Examples include the sensitising dyes described in US 5,200,292. Thus, suitable sensitising dyes include cationic dye/anionic borate dye complexes represented by the general formula (I):



(I)

wherein D^+ represents a cationic dye; and R_1, R_2, R_3 and R_4, which may be the same or different, each represents an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group, an unsubstituted or substituted aralkyl group, an unsubstituted or substituted alkenyl group, an unsubstituted or substituted alkynyl group, an unsubstituted or substituted alicyclic group, or an unsubstituted or substituted heterocyclic group.

Examples of the cationic dyes which can be used in the present invention include cyanine dyes and dyes comprising a cation portion such as a quaternary

ammonium ion covalently bonded to other neutral dye structures via a bonding group.

Cationic dye/borate anion complexes are known in the art. Examples of methods for the preparation of these complexes and the use of these complexes in an image formation system are described in U.S. Pat. Nos. 3,567,453, 4,307,182, 4,343,891, 4,447,521, 4,450,227, and 5,200,292.

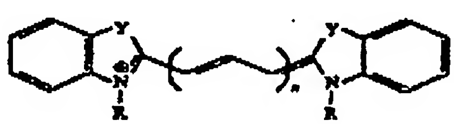
For example the cationic dye/borate anion complex which can be used in the present invention can be prepared by allowing a borate salt and a dye to react in a known counter ion exchange process. This process is further disclosed in Hishiki, Y., *Repts. Sci-Research Inst.* (1953), 29, pp 72 to 79. Examples of useful borate salts include sodium salts such as sodium tetraphenyl borate, sodium triphenyl butyl borate and sodium trianisyl butyl borate, and ammonium salts such as tetraethyl ammonium tetraphenyl borate.

Examples of useful cationic dyes to be used in the present invention include photo-reducible cationic dyes capable of forming a complex which is stable in a dark place with a borate anion, such as cationic methine, polymethine, triarylmethane, indoline, thiazine, xanthene, oxazine and acridine dyes. More particularly, these dyes are cationic, carbocyanine, hemicyanine, rhodamine and azomethine dyes.

Specific examples of such dyes include methylene blue, safarine O, malachite green, cyanine dyes of the

general formula (II) and rhodamine dyes of the general formula (III) (e.g., Rhodamine B or Rhodamine 6G).

Cationic cyanine dyes disclosed in US-A-3,495,987 and US-A-5,200,292 are believed to be useful in the present invention.



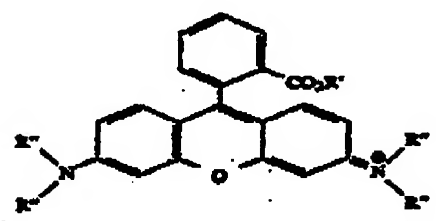
(II)

wherein n represents 0 or an integer of 1 to 3; R represents an alkyl group; and Y represents CH-CH, $N\text{-}CH_3$, $C(CH_3)_2$, O, S or Se.

In the general formula (II), R is preferably a lower alkyl group (preferably having 1 to 8 carbon atoms) or an alkyl group (preferably having 1 to 5 carbon atoms) substituted by at least one of a carboxyl group, a sulfo group (itself optionally substituted by, for example, a hydroxy group or a halogen atom), a hydroxyl group, a halogen atom, an alkoxy group having 1 to 4 carbon atoms (itself optionally substituted by, for example, one or more alkoxy groups having 1 to 4 carbon atoms or sulfoalkoxy groups having 1 to 4 carbon atoms), a phenyl group or a substituted phenyl, for example, β-sulfoethyl, γ-sulfopropyl, γ-sulfobutyl, δ-sulfobutyl, 2-[2-(3-sulfopropoxy)ethoxy]ethyl,

2-hydroxysulfopropyl, 2-chlorosulfopropyl, 2-methoxyethyl, 2-hydroxyethyl, carboxymethyl, 2-carboxyethyl, 2,2,3,3'-tetrafluoropropyl, 3,3,3-trifluoropropyl or trifluoroethyl.

(III)



wherein R' and R" each represents a hydrogen atom, an alkyl group (preferably having 1 to 6 carbon atoms), an aryl group or combination thereof, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, phenyl, benzyl, etc.

The borate anion used in the present invention is so designed that a borate radical produced by the transfer of an electron to a dye upon exposure to light easily dissociates into a radical as follows:

$$BR_4^{\cdot} \rightarrow BR_3 + R^{\cdot}$$

For example, triphenylbutyl borate anion and trianisylbutyl borate anion easily dissociate into triphenyl boran or trianisyl boran and a butyl radical. Thus, these anions are particularly preferred anions. On the other hand, tetrabutyl borate anion does not easily dissociate probably

because a tetrabutyl borate radical produced therefrom is so unstable that it accepts an electron from a dye. Similarly, tetraphenyl borate anion functions poorly because it cannot easily produce a phenyl radical.

In the borate anion represented by the general formula (I), one or two of R_1, R_2, R_3 and R_4 are preferably alkyl groups. R_1, R_2, R_3 and R_4 each may contain 20 or less carbon atoms, preferably 1 to 7 carbon atoms. A preferable combination of R_1, R_2, R_3 and R_4 is one or more alkyl groups and one or more aryl groups, or one or more alkyl groups and one or more aralkyl groups. Particularly, a combination of three aryl groups and one alkyl group is most preferred.

Typical examples of alkyl groups represented by R_1, R_2, R_3 and R_4 include methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl and stearyl groups. Such an alkyl group may be substituted by one or more halogen atoms, one or more cyano, acyloxy, acyl, alkoxy or hydroxy groups.

Typical examples of aryl groups represented by R_1, R_2, R_3 and R_4 include phenyl, naphthyl, and substituted aryl groups such as anisyl, and alkaryl such as methyl phenyl and dimethyl phenyl.

Typical examples of aralkyl groups represented by R_1, R_2, R_3 and R_4 include benzyl and phenethyl groups. Typical examples of alicyclic groups represented by R_1, R_2, R_3 and R_4 include cyclobutyl, cyclopentyl and cyclohexyl groups. Examples of unsubstituted alkynyl

groups represented by R_1, R_2, R_3 and R_4 include propynyl and ethynyl groups. Examples of substituted alkynyl groups represented by R_1, R_2, R_3 and R_4 include a 3-chloropropynyl group. Examples of unsubstituted alkenyl groups represented by R_1, R_2, R_3 and R_4 include propenyl and vinyl groups. Examples of substituted alkenyl groups represented by R_1, R_2, R_3 and R_4 include 3-chloropropenyl and 2-chloroethenyl groups. Examples of unsubstituted heterocyclic groups represented by R_1, R_2, R_3 and R_4 include 3-thiophenyl and 4-pyridinyl groups. Examples of substituted heterocyclic groups represented by R_1, R_2, R_3 and R_4 include a 4-methyl-3-thiophenyl group.

In general, useful cationic dye/borate anion complexes must be empirically confirmed. A combination of a cationic dye and a borate anion having a useful possibility can be fixed by Weller's equation (Rehm, D. and Weller, A., Isr. J. Chem., (1970), 8, pages 259 to 271). The equation can be simplified as follows:

$$\Delta G = E_{ox} - E_{red} - E_{kv}$$

wherein ΔG represents the change in Gibbs' free energy; E_{ox} represents the oxidation potential of borate anion $BR_4{}^{\prime\prime\prime}$-; E_{red} represents the reduction potential of an anionic dye; and E_{kv} represents the energy of light used for the excitation of the dye.

It is believed that a useful complex has a negative free energy change. Similarly, the difference in the

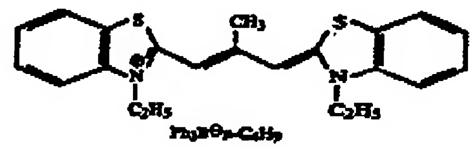
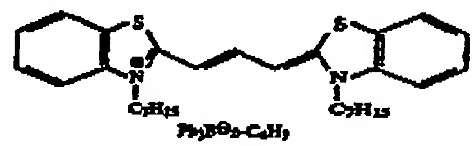
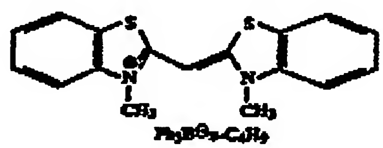
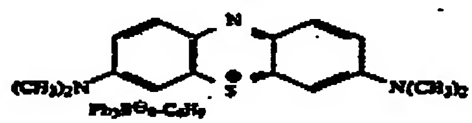
reduction potential of the dye and the oxidation potential of borate must be negative with respect to a complex which is stable in a dark place.

Namely,

$$E_{ox}-E_{red}>0$$

As previously mentioned, this is a simplified equation and thus does not absolutely predict if a complex is useful in the present invention. There are many other factors which affect such a decision. One of these factors is the effect of the use of a monomer on a complex. It is known that if Weller's equation gives an excessive negative value, there can be some deviation from the equation. Thus, this equation is only a first approximation.

Particular examples of cationic dye/borate anion complexes believed useful in the present invention will be shown hereafter together with their λ_{max}.

Complex No.	Structure	λ_{max}
1		552 nm
2		568 nm
3		492 nm
4		422 nm
5		458 nm

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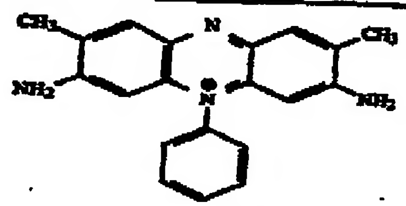
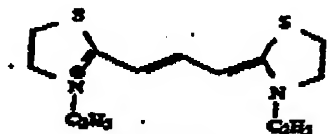
6 525 nm



$Ph_3B^{\ominus}n\text{-}C_4H_9$

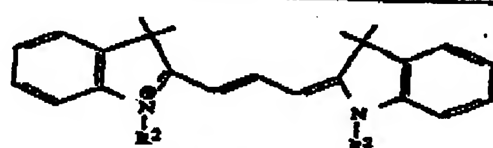
7 430 nm



$Ar_3B^{\ominus}—R^1$

No.	R^1	Ar
7A	n-Butyl	Phenyl
7B	n-Hexyl	Phenyl
7C	n-Butyl	Anisyl

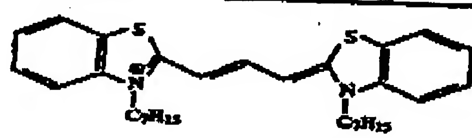
8 550 nm

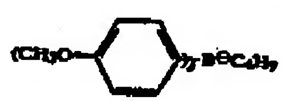


$Ar_3B^{\ominus}—R^1$

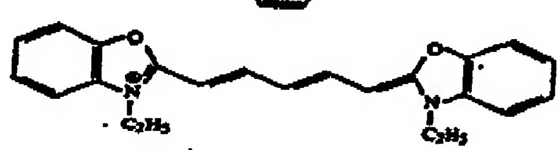
No.	R^2	R^1	Ar
8A	Methyl	n-Butyl	Phenyl
8B	Methyl	n-Hexyl	Phenyl
8C	n-Butyl	n-Butyl	Phenyl
8D	n-Butyl	n-Hexyl	Phenyl
8E	n-Heptyl	n-Butyl	Phenyl
8F	n-Heptyl	n-Hexyl	Phenyl
8G	Ethyl	n-Butyl	Phenyl

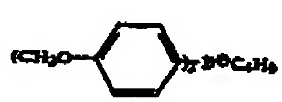
9 570 nm





10 590 nm





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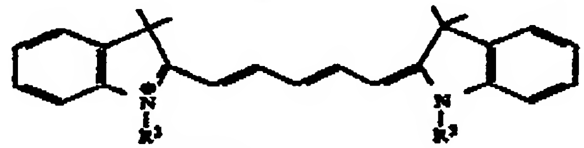
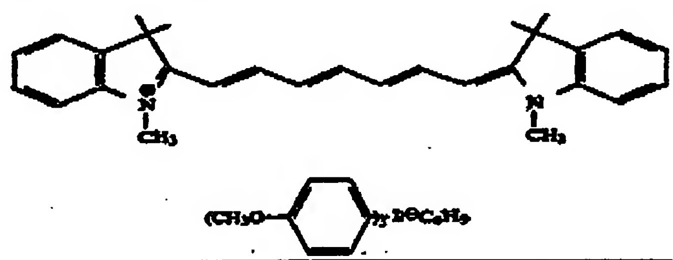
11 640 nm



$Ar_3B^{\ominus}—R^1$

No.	R^3	R^1	Ar
11A	Methyl	n-Butyl	Phenyl
11B	Methyl	n-Hexyl	Phenyl
11C	n-Butyl	n-Butyl	Phenyl
11D	n-Butyl	n-Hexyl	Phenyl
11E	n-Pentyl	n-Butyl	Phenyl
11F	n-Pentyl	n-Hexyl	Phenyl
11G	n-Heptyl	n-Butyl	Phenyl
11H	n-Heptyl	n-Hexyl	Phenyl
11J	Methyl	n-Butyl	Anisyl

Complex No.	Structure	λ_{max}
12		740 nm

In accordance with a further aspect of the present invention there is provided a method of cleaning a surface comprising the steps of:

contacting the surface with a cleaning composition of the invention as defined above thereby depositing a residue of the photocatalytic material on the surface; and

allowing the photocatalytic material to catalyse or

effect oxidation, reduction or other decomposition and/or to facilitate release of soils present on or subsequently deposited on the surface.

The method is suitably carried out with the surface and the cleaning composition at ambient temperature and without any subsequent heat treatment.

The photocatalytic material in the composition and method of the present invention preferably comprises or includes titanium dioxide, zinc oxide or a combination of the two, and is preferably present in an amount of from 0.01% to 20%, especially 0.2% to 3% by weight of the composition. Titanium dioxide is preferred. Most preferred is titanium dioxide in anatase form.

The composition of the present invention may be provided in any appropriate form such as, for example, a liquid, cream, mousse, emulsion, microemulsion or gel form and may be dispensed in conventional manner directly from a bottle or by means of, for example, a pump or trigger spray or an aerosol.

Whilst the person skilled in the art will be able to prepare aqueous and non-aqueous formulations tailored to the above dispensing forms, the compositions of the present invention generally comprise not more than 99.7%, preferably 75% to 95% water, and anionic, non-ionic or amphoteric surfactants, or compatible combinations thereof, in an amount of 0.05% to 80%, typically 0.5% to 10%. Examples of nonionic

surfactants which may be employed in the compositon include those which are water soluble or water miscible and include but are not limited to one or more of the following: amine oxides, block copolymers, alkoxylated alkanolamides, ethoxylated alcohols, and ethoxylated alkyl phenols, and the like. Suitable anionic surfactants include, but are not limited to: alkali metal salts, ammonium salts, amine salts, aminoalcohol salts or the magnesium salts of one or more of the following compounds: alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylarly polyether sulfates, monoglyceride sulfates, alkylsufonates, alkylamide sulfonates, alkylarylsulfonates, olefinsulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkylsulfosuccinamate, alkyl sulfoacetates, alkyl phosphates, alkyl ether phosphates, acryl sarconsinates, acyl isethionates, and N-acyl taurates. Generally, the alkyl or acyl radical in these various compounds comprise a carbon chain containing 12 to 20 carbon atoms. Further exemplary anionic surfactants which may be used include fatty acid salts, inlcuding salts of oleic, ricinoleic, palmitic, and stearic acids; copra oils or hydrogenated copra oil acid, and acyl lactylates whose acyl radical contains 8 to 20 carbon atoms. Grease cutting, surfactant synergistic or other solvents may also be included generally in amounts of not more than 99%, typically not more than 50%. Other known ingredients such as antimicrobial agents, suspending agents, colourants, perfumes, thickeners, preservatives and the like may be included

in conventional quantities. In particular variations of the compositions of the invention, some or all of the ingredients may be of high volatility whereby a residue of photocatalytic material can be left behind on a surface in a controlled manner.

In another preferred variation of the invention, the photocatalytic material may be doped with an additional element which has the effect of reducing the energy required to promote an electron of the photocatalytic material to the conductance band, leaving the corresponding hole in the valence band.

It is readily apparent that the residue of photocatalytic material deposited by the composition of the invention should preferably be imperceptible or almost imperceptible to the user. Preferably, the photocatalytic material used in the present invention is of a microscopic particle size. The microscopic particle size also assists in achieving a uniform dispersion throughout the formulation and in maximising the efficiency of the photocatalytic reaction. Suitably the photocatalytic material has a mean particle size of at least 0.1 nm, preferably at least 0.5 nm, most prefereably at least 2 nm. Suitably the photocatalytic material has a mean particle size less than 20μm, preferably less than 1μm, most preferably less than 0.1 μm. Especially preferred is a photocatalytic material having a mean particle size in the range 5-20 nm.

The following examples are illustrative of

compositions according to the invention in the form of a liquid. They may all contain sensitising dyes, colorant dyes, fragrances and preservatives, preferably at concentrations not more than 1% each, with the balance of the formulations being water.

Titanium dioxide has a mean particle size of about 10 nm, in these examples.

All percentages in this specification are expressed in weight of component per total weight of composition (that is w/w) unless otherwise stated.

To formulate a composition a commercially available surfactant-stabilized colloidal aqueous solution of titanium was blended at ambient temperature with the other materials described below, in water.

To test a composition it was applied to a glass surface on which kitchen soils were present. The soils were successfully removed and a layer of titanium dioxide was deposited and the thickness and refractive index measured by ellipsometry. The surface was then re-soiled with kitchen soils and allowed to dry for 5 minutes. The thickness and refractive index of the new layer of kitchen soiling was noted through ellipsometry. This was carried out in duplicate, one glass surface left for a period of 1 day in a controlled lighting environment, the other surface acting as the first control being left for a period of 1 day in darkness.

As a second control, a clean, uncontaminated glass surface was also soiled at this time with the same kitchen soils and allowed to dry for 5 minutes. This surface was measured for thickness and refractive index using ellipsometry then this surface was left for a period of 1 day. After this time the surfaces were examined and decomposition of the soils was assessed on the basis of the difference between the controls and test slide. By this method the compositions described herein were found to be effective in combating soils.

EXAMPLE 1

Ethoxylated alcohol	1%
Disodium cocoamphodiacetate	0.2%
Sodium lauryl sulphate (28% active contact)	1%
Propylene glycol n-butyl ether	3%
Xanthan gum	1%
Titanium dioxide (mainly anatase form)	0.5%
Sensitising dye - complex no. 1 defined above	0.001%

EXAMPLE 2

Non-ionic surfactant	1%
Amphoteric surfactant	0.2%
Anionic surfactant	1%
Propylene glycol n-butyl ether	3%
Bentonite clay	1%
Zinc oxide	1.0%

Sensitising dye - complex no. 8E defined above	0.002%

The following example is illustrative of a compositions according to the invention in the form of a cream. It may contain a dye, fragrance and preservative at concentrations not more than 1% each with the balance of the formulation being water.

EXAMPLE 3

Chalk	9%
Titanium dioxide (mainly in rutile form)	1%
Sodium lauryl sulphate (28% active content)	2%
Monoethanolamine	0.4%
Cyclodimethicone/dimethicone	9%
Poly dimethylsiloxane	0.5%
Sensitising dye - complex no. 10 defined above	0.0005%

The following example is illustrative of a composition according to the invention in the form of a mousse from an aerosol. It may contain a dye, fragrance and preservative at a maximum concentration of 1% each with the balance of the formulation being water.

EXAMPLE 4

Aminomethylpropanol	0.5%
Ammonium hydroxide	0.5%
Butane	10%

Benzalkonium chloride	0.5%
Ethanol	2%
Morpholine	0.5%
PP3 methyl ether	8%
Trideceth 7	1%
Titanium dioxide (mainly in anatase form)	1%
Sensitising dye - complex no. 8E defined above	0.001%

CLAIMS

1. A cleaning composition which includes a photocatalytic material able to combat soils or a precursor to such a photocatalytic material, and a sensitising dye which acts to absorb visible or ultra violet radiation and improve the efficacy of the photocatalytic material in combating soils.

2. A composition according to claim 1 wherein the photocatalytic material is titanium dioxide and/or zinc oxide.

3. A composition according to claim 2 wherein the photocatalytic material is titanium dioxide.

4. A composition according to claim 1, 2 or 3 wherein the photocatalytic material comprises particles having a size imperceptible or almost imperceptible to the eye when deposited on the surface.

5. A composition according to claim 4 wherein the particles have a mean size of from 3 nm to 20 μm.

6. A composition according to claim 5 wherein the particles have a mean size of less than 1μm.

7. A composition according to any preceding claim, which composition comprises one or more

surfactants.

8. A composition as claimed in any preceding claim, which composition comprises one or more solvents able to assist in removal of soils.

9. A composition as claimed in any preceding claim, which composition comprises one or more ingredients selected from antimicrobial agents, suspending agents, colourants, perfumes, thickeners and preservatives.

10. A composition as claimed in any preceding claim wherein the dye constitutes up to 1% of the weight of the composition.

11. A cleaning composition which comprises:
a) a photocatalytic material able to combat soils or a precursor to such a photocatalytic materaial; and
b) a sensitising dye which is capable of absorbing radiation of a first wavelength from sunlight and emitting radiation of a second wavelength which enhances the cleaning effect of the photocatylic material.

12. A method of cleaning a surface comprising the steps of contacting the surface with a composition as claimed in any preceding claim thereby depositing a residue of the photocatalytic material on the surface and allowing the photocatalytic material to

catalyse or effect an oxidation, reduction or other decomposition of soils present or subsequently deposited on the surface.

13. A method as claimed in claim 12 wherein the decompositon of the soils involves a free radical reaction.

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26

Application No:	GB 9930253.1	**Examiner:**	Michael Conlon
Claims searched:	1 - 13	**Date of search:**	30 March 2000

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C5D D105

Int Cl (Ed.7): C11D 3/12 7/20

Other: Online: WPI EPODOC PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	WO96/23051 A1 (Rhone Poulenc)	1
A	US4731194 (Henkel)	1
A	Derwent Abstract No.1997-498579 [46] relating to JP920035596 (Neos) 09.09.97	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.